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Application No. : 10/688,118
Inventor(s) : Kenneth D. Vinson
Filed : October 17, 2003
Art Unit : 1731
Examiner : Dennis R. Cordray
Docket No. : 9066M2
Confirmation No. : 9231
Customer No. : 27752
Title : PAPER SOFTENING COMPOSITIONS CONTAINING
LOW LEVELS OF HIGH MOLECULAR WEIGHT
POLYMERS AND SOFT TISSUE PAPER PRODUCTS
COMPRISING SAID COMPOSITIONS

DECLARATION UNDER 37 CFR 1.132

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Alexandria, VA 22313-1450

INTRODUCTORY REMARKS

Dear Sir:

I, Kenneth Douglas Vinson, hereby declare the following:

1. THAT, I am a named inventor of the above-identified patent application;
2. THAT, I received Bachelor of Science Degree in Chemical Engineering from The University of Tennessee in 1977 and have been employed by The Procter & Gamble Company, as a Research Fellow assigned primarily to Procter & Gamble's Paper Softeners project, the subject of the present application, since June 1999.
3. THAT, I am familiar with International Application No. WO 02/48458 A1 to Barnholtz et al. ("Barnholtz") and U.S. Patent 3,624,019 to Anderson et al. ("Anderson"). I have thoroughly reviewed Barnholtz and Anderson and it is my technical opinion that

Appl. No. 10/688,118
Docket No. 9066M2
Reply to Advisory Action mailed on 07/21/06
Customer No. 27752

Barnholtz in view of Anderson fails to adequately teach the addition of a water-in-oil emulsion into an oil in water emulsion.

Barnholtz teaches a softening composition comprising an oil-in-water emulsion. The emulsion of Barnholtz has certain extensional viscosity characteristics which he teaches may be obtained by including a high molecular-weight polymer in the emulsion. Anderson teaches a method of forming a solution of a water soluble polymer by inverting a water-in-oil emulsion comprising the polymer into an aqueous medium. According to Anderson, the aqueous medium can contain materials other than water; however, he teaches only single-phase media, i.e. water and, optionally, water soluble substances. For example, Anderson teaches the use of water-soluble surfactants in the water; wherein the surfactants aid in drawing the polymer out of the discontinuous particles of the water-in-oil emulsion into the continuous phase of the water to which it is being added.

One skilled in the art would not be able to use the teachings of Anderson to arrive at the subject invention. Anderson only teaches inverting the polymer emulsions into water. He teaches that the water may be modified to aid in forming the emulsion; however his teaching is directed at adding the water-in-oil emulsion to a single phase aqueous medium, i.e. either pure water or water which has been modified by adding water soluble materials. Since Barnholtz is an oil-in-water emulsion, one would not expect that following the procedures of Anderson would result in a successful inversion since Anderson is limited to the teaching inversion of water-in-oil emulsions into single-phase media. It is not obvious that the inversion procedure taught by Anderson would be effective to invert a water-in-oil emulsion into an already-formed oil-in-water emulsion. The presence of the oil phase in the destination media would be expected to interfere with the inversion by e.g. reducing the water activity available to invert the emulsion. Phase inversion is well known to require a certain threshold quantity of water; for example, Section 3.2 of the attached Miller publication (Miller, D. J.; Henning, T.; Grunbein, W; Phase inversion of W/O emulsions by adding hydrophilic surfactant – a technique for making cosmetic products, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Volumes 183-185, 15 July 2001, pp. 681-688, p. 687) describes how phase inversion takes place only after certain critical quantities of water are added to a water-in-oil emulsion.

I, being of at least ordinary skill in the art of paper softening, am not able to use the teaching of Barnholtz combined with Anderson to make a composition suitable for atomizing without excessive aerosolization in the form of an oil in water emulsion

Page 2 of 3

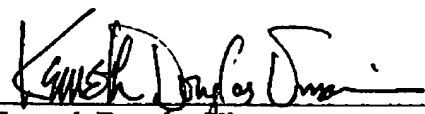
Appl. No. 10/688,118
Docket No. 9066M2
Reply to Advisory Action mailed on 07/21/06
Customer No. 27752

comprising: a continuous aqueous phase and a discontinuous oil phase wherein the rheology of the aqueous phase is modified by the addition of a water-in-oil emulsion comprising: a high molecular weight polymer in a discontinuous aqueous phase and a continuous organic solvent phase. Anderson only teaches the inversion of a water-in-oil emulsion into a single phase aqueous media such as pure water or a water solution (Anderson, Col. 4, lines 3-14), and thus cannot be properly combined with Barnholtz.

4. THAT, with regard to the claimed invention of the above-named application, I submit that I and my co-inventors have unexpectedly found that a softening composition suitable for atomizing without excessive aerosolization can be produced by inverting a water-in-oil emulsion, comprising a high molecular weight polymer in a discontinuous aqueous phase, and a continuous organic solvent phase into an oil-in-water emulsion comprising a continuous aqueous phase and a discontinuous oil phase. Before my discovery and invention, no one had taught such a composition.

I, Kenneth Douglas Vinson, declare that all statements made herein are true to the best of my knowledge, or if made upon information and belief, are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both under Section 1001 of Title 18 of the United States Code and that such willful false statements my jeopardize the validity of the application or any patent issued thereon.

Further Declarant sayeth naught.


Kenneth Douglas Vinson

Date: 25 August 2006



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Colloids and Surfaces

A: Physicochemical and Engineering Aspects 183–185 (2001) 681–688

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Phase inversion of W/O emulsions by adding hydrophilic surfactant — a technique for making cosmetics products

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Abstract

W/O emulsions can be inverted to O/W systems by adding hydrophilic emulsifier. This has been studied with the emulsifier combination rapeseed sorbitol ester (hydrophobic) and lauroyl glutamate (hydrophilic). Phase inversion occurs at a well defined amount of hydrophilic emulsifier. This critical quantity of hydrophilic emulsifier depends on the emulsion recipe, in particular the water/oil ratio. Stable O/W model cosmetics emulsions can be made by this method. Unlike the PIT emulsification technique, temperature dependent surfactant properties are not required, so this method can also be used with non-ethoxylated emulsifiers. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Emulsions; Cosmetics; Phase inversion; Sorbitol ester; Acyl glutamate

1. Introduction

Emulsions are widely used in skin care products. Formulators have known for many years that adjusting the hydrophile/lipophile balance of the emulsifier is a key aspect for achieving emulsion stability [1,2]. It is now realised that the effective hydrophile/lipophile balance depends not only on the structure of the emulsifier but also on the temperature, oil type and salinity [3]. Changing these parameters allows the surfactant to be systematically varied from predominantly oil-soluble to predominantly water-soluble. At a particular point the properties are balanced (optimum

oil–water–emulsifier system). This correlates with low interfacial tension, low curvature of the surfactant layer and roughly equal partitioning of surfactant between oil and aqueous phases. At the optimum a surfactant-rich microemulsion in equilibrium with the oil and water phases may be formed, but this is not always so [4].

The phase inversion temperature (PIT) concept has proved fruitful from both theoretical and practical points of view. Ethoxylate emulsifiers are temperature sensitive, becoming less hydrophilic on heating. Emulsions stabilised by them generally show a reversible O/W → W/O transition at a well-defined temperature, the PIT. Cosmetics O/W emulsions with improved stability and small droplet size can be manufactured by producing a W/O emulsion at high temperature and cooling through a phase inversion [5]. The system is adjusted to give a PIT well above ambient tempera-

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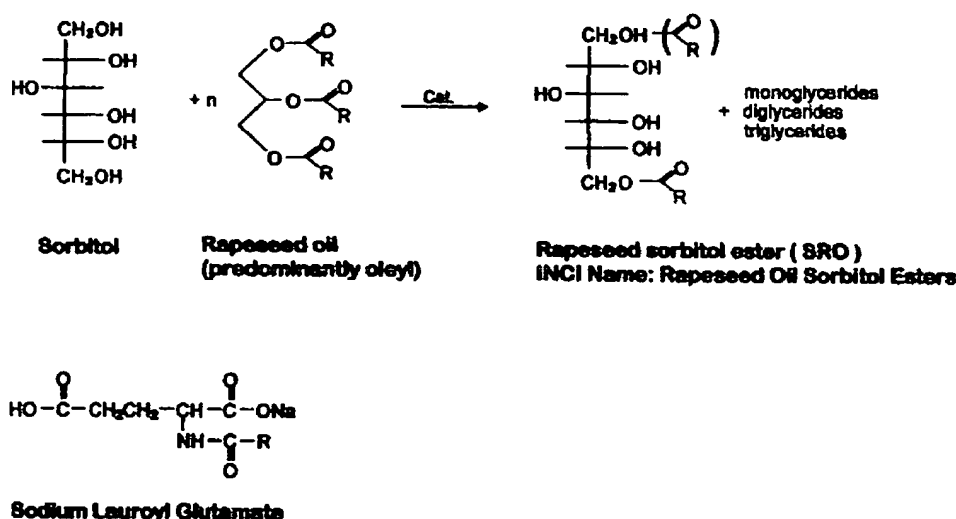


Fig. 1. Structure of emulsifiers.

ture, as the stability is reduced if the phase inversion is too close to the storage temperature.

The PIT method is confined to ethoxylated surfactants, as other types do not show a sufficiently large change in surfactant properties with temperature. An equivalent to the PIT method at constant temperature would involve changing the chemical composition of the system so as to pass through an optimum. In the present work we have explored this type of technique by using a hydrophobic/hydrophilic emulsifier combination and varying the ratio of the two components. The hydrophobic emulsifier, a rapeseed sorbitol ester (SRO), is a W/O emulsifier. Sodium lauroyl glutamate, the hydrophilic component, is a surfactant used in cosmetic cleansers. Though it is not by itself an effective emulsifier, we have found it to be a useful component for adjusting the properties of emulsifier mixtures.

Hydrophobic/hydrophilic emulsifier combinations are also used in the preparation of multiple emulsions [6–8]. Usually this involves dispersing a W/O emulsion into an aqueous solution of a hydrophilic emulsifier. If conditions are not optimised, phase inversion may occur instead of multiple emulsion formation.

2. Materials and methods

Both emulsifiers are commercial products. SRO, which is produced by catalytic reaction of rapeseed oil and sorbitol, contains both mono- and diesters, together with some transesterification products. It is a liquid miscible with oils but not soluble in water. Sodium lauroyl glutamate is a water soluble surfactant. Although the disodium salt is the commercially available form, it should be remembered that the pH of skin care products is typically about 5.5. In these weakly acidic conditions, the monoacid is the predominant species. The structures of the emulsifiers are shown in Fig. 1.

Table 1
Model cosmetic oil

Oil I	
Component	%
Isopropyl palmitate	30
Soja oil	20
Paraffin oil	50

Table 2
Recipes for test emulsions

	(a) See Fig. 5	(b) See Fig. 6
Emulsifier mixture	2.0%	2.0%
Oil I	45.4%	22.5%
Water + HCl*	52.6%	75.3%
Polyacrylate	—	0.2%
Procedure	Disperse the emulsifier mixture in oil and stir in water + HCl	Disperse SRO in oil. Stir in water + HCl + lauroyl glutamate. Then stir in polyacrylate as a 1% half-neutralised solution

* The amount of HCl used is sufficient to give a final pH value of 5.

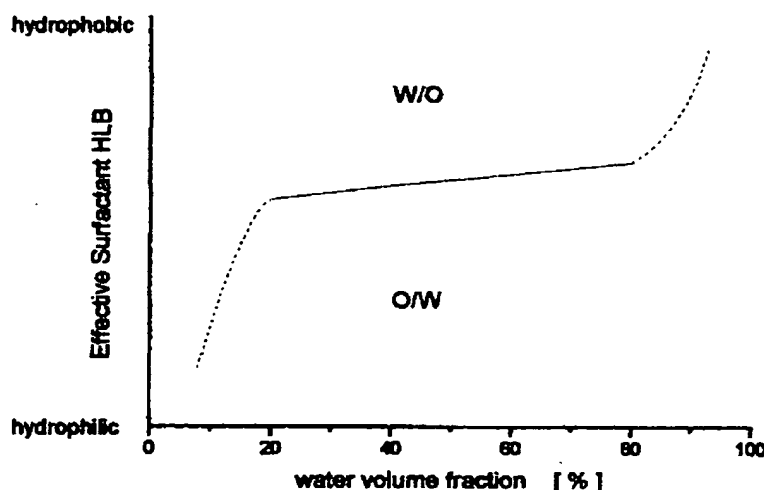


Fig. 2. Phase inversion map (schematic). Full line, transitional inversion; Dashed line, catastrophic inversion.

The model cosmetic oil Table 1 has been given the same designation as in previous work [9].

Emulsions were made by stirring at moderate shear in a beaker (10 min at 250 rpm with a four blade stirrer). Further details of the emulsification technique are given in Table 2.

For the titration method of determining phase inversion, a W/O emulsion was prepared with SRO as emulsifier. Then a 10% solution of the lauroyl glutamate (neutralised to pH 5.5 with HCl) was added in small portions. At 60 s after each addition, the stirrer was switched off and the electrical conductivity measured. Phase inversion could be

recognized from the large increase in conductivity.

Particle sizes were measured by laser diffraction with a Malvern Mastersizer.

3. Theoretical background

3.1. Types of phase inversion

The relationship between emulsion type, phase ratio and surfactant properties can be described by a diagram of the type introduced by Salager [10]. Such a phase inversion map is shown in Fig. 2.

Over a broad range of water/oil ratios, the phase inversion is caused by the change in surfactant hydrophile/lipophile properties (full line). With some systems, there are three phases in equilibrium in the inversion region, most of the

surfactant being in a surfactant-rich phase. In such cases the inversion is reversible. At inversion there is usually a viscosity minimum and fast phase separation is observed if the system is allowed to stand. This type of phase inversion is

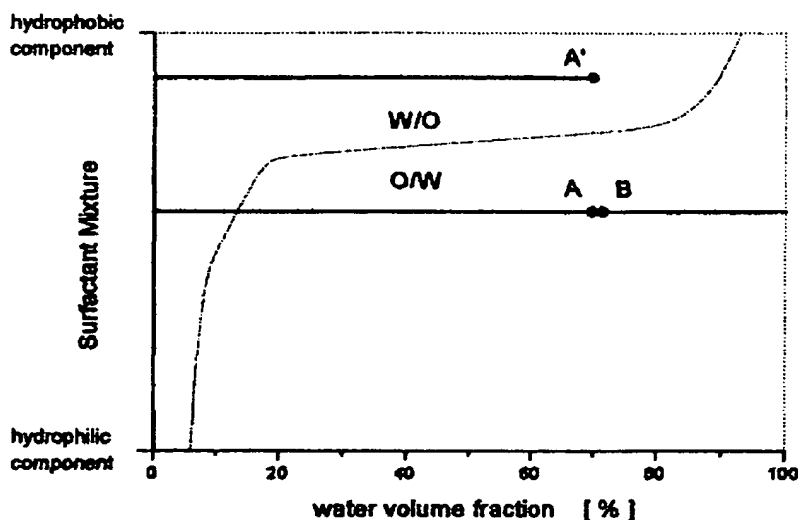


Fig. 3. Emulsification techniques at constant emulsifier composition. A, A', water added to oil + surfactant; B, oil + surfactant added to water. Dashed line is locus of phase inversion.

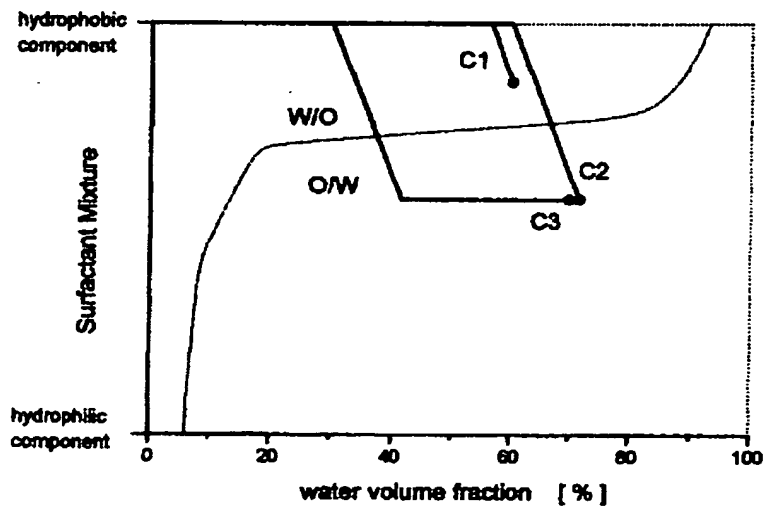


Fig. 4. Emulsification techniques at variable emulsifier composition. See text for discussion of paths C1, C2, C3.

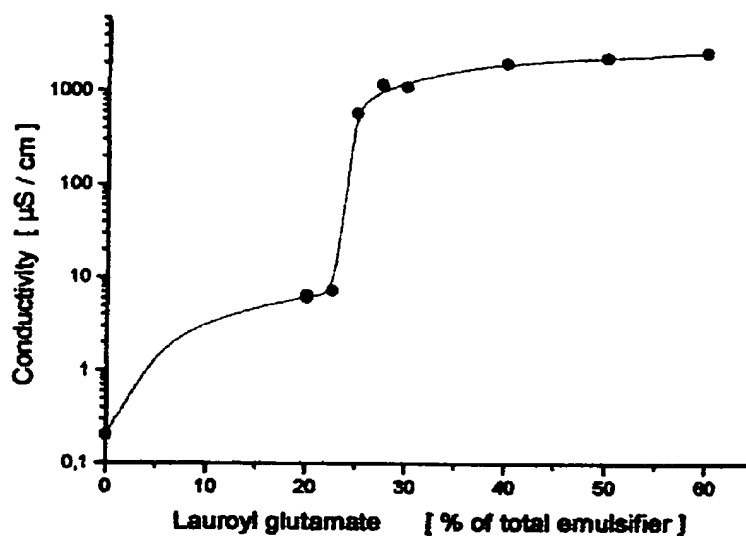


Fig. 5. Electrical conductivity of emulsions as a function of lauroyl glutamate content. Emulsions contain equal volumes of oil and aqueous phase. Recipe details: see Table 2(a).

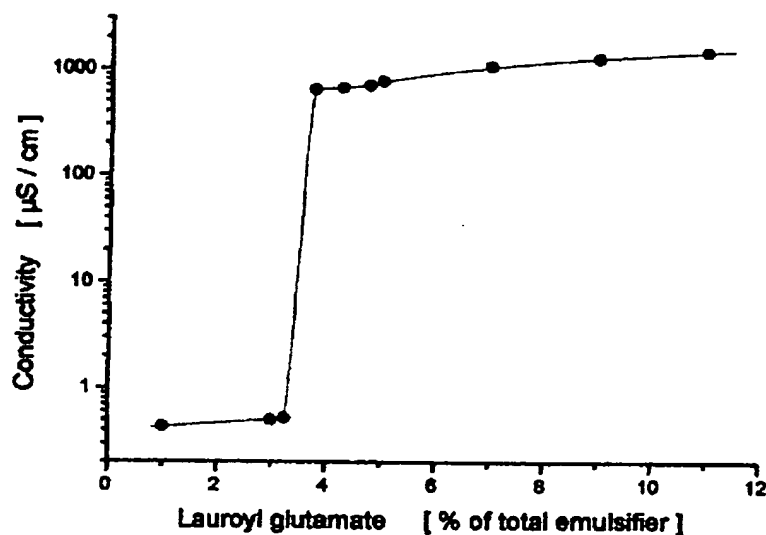


Fig. 6. Electrical conductivity of emulsions as a function of lauroyl glutamate content. Model cosmetic emulsions with 22% oil. Recipe details: see Table 2(b).

used in PIT emulsification; the surfactant phase may be a bicontinuous microemulsion or a liquid crystal [11].

Phase inversion caused by changes in surfactant properties may also proceed without formation of a third phase at equilibrium. This behaviour is

emulsions (which obey Bancroft's rule) are of the type favoured by the surfactant hydrophile/lipophile properties, abnormal ones are of the reverse type. At very high internal phase volumes the normal emulsion becomes unstable and inverts. Usually there is a viscosity maximum at the inversion. If normal \rightarrow abnormal and abnormal \rightarrow normal transitions are compared, considerable hysteresis is observed [13].

Phase inversion in emulsions has been treated theoretically using catastrophe theory [13,14] and by kinetic models [15]. On this view one can distinguish between two types:

- transitional: smooth change in properties, reversible
- catastrophic: discontinuity in properties, with pronounced hysteresis.

In Fig. 2 the full line is generally considered to be a transitional inversion and the dashed lines catastrophic ones. This classification is based mainly on work with emulsions that invert via a three phase system and it is unclear to what extent transitional inversions occur without formation of a surfactant-rich phase.

3.2. Emulsification techniques

Emulsification methods can be considered in terms of paths on the phase inversion map.

In Fig. 3 we show schematically two standard techniques. Path A involves dissolving both emulsifiers in the oil phase and adding water. Initially a W/O emulsion is formed. When enough water has been added it undergoes catastrophic inversion to an O/W system which is the preferred type. Path B is the reverse: oil + emulsifier is added to water. The final composition is the same, but no phase inversion is involved. Also shown is A', a modification of A with insufficient hydrophilic emulsifier to give an O/W emulsion.

Fig. 4 shows how the surfactant composition can be varied to control phase inversion. The hydrophobic emulsifier is used to prepare a W/O emulsion and then an aqueous solution of hydrophilic emulsifier is added. At low concentrations of hydrophilic emulsifier the system remains W/O (C1). With sufficient hydrophilic emulsifier an inversion to O/W occurs (C2). The water/oil

ratio at which phase inversion occurs can be controlled; paths C2 and C3 give the same final composition, but with C3 the phase inversion is at a lower content of internal phase.

4. Results and discussion

4.1. Surfactant composition for emulsion inversion

As a first test of the amount of acyl glutamate required to stabilise an O/W emulsion with SRO as main emulsifier, we made emulsions containing equal volumes of oil and water (Table 2(a)). A sharp transition from W/O to O/W when the emulsifier contains 22% acyl glutamate is shown by a jump in conductivity (Fig. 5).

In a second set of experiments the oil content was reduced to an amount typical for a cosmetic O/W formulation and some polymeric thickener added to improve stability (Table 2(b)). Again we find a well-defined transition from W/O to O/W, but it occurs at considerably lower amounts of lauroyl glutamate (Fig. 6). As Fig. 7 shows, the stability of the O/W emulsion is best very near the transition point; this corresponds to the smallest droplet sizes.

The amount of lauroyl glutamate required for phase inversion was studied in more detail by a titration method. First, a W/O emulsion was prepared using the hydrophobic emulsifier. Then hydrophilic surfactant was gradually added until phase inversion occurred. The experiment was repeated for various amounts of water in the initial W/O emulsion, keeping the ratio of hydrophobic emulsifier to oil constant. Compositions at the inversion point are shown in Fig. 8 where we have plotted the fraction of hydrophilic surfactant in the emulsifier mixture against the fraction of oil phase. More hydrophilic emulsifier is required at larger amounts of oil, suggesting that the SRO becomes more hydrophobic. Partitioning of hydrophobic components into alkanes generally makes surfactants more hydrophilic which would suggest the opposite trend, [16,17]. However, with some polar oils PTT studies show that the surfactant becomes more hydrophobic at higher oil contents [17].

At large fractions of oil phase, where more acyl glutamate is needed, the O/W emulsion was unstable even near the inversion point. Thus for maximum stability, conditions should be chosen so that only small amounts of lauroyl glutamate are used. However, a minimum amount of the hydrophilic surfactant is probably required to prevent slow partial re-inversion giving a mixed O/W–W/O emulsion.

4.2. Inversion type

The reversibility of the inversion was tested by adding hydrophobic emulsifier after the inversion point was reached. Even with quite large amounts of SRO the system did not invert back to a W/O emulsion.

4.3. Particle sizes

Emulsions produced by our phase inversion technique generally gave droplet sizes in the 20 μ region. However, we have observed much smaller droplets ($\leq 1 \mu$ diameter) in some cases. Preliminary work indicates that a critical emulsifier concentration, together with optimisation of the emulsifier system is required to achieve these fine emulsions.

5. Conclusions

O/W emulsions can be prepared by first making a W/O emulsion with a hydrophobic emulsifier and then adding a hydrophilic surfactant to invert it. Unlike the PIT method, this does not require temperature dependent emulsifier properties.

With rapeseed sorbitol ester/lauroyl glutamate as the emulsifier combination, phase inversion takes place at a well defined amount of the hydrophilic surfactant. Less hydrophilic surfactant is required the higher the oil content at inversion. A titration technique can be used to determine the critical amount of hydrophilic surfactant; this is useful for formulation work.

The W/O \rightarrow O/W phase inversion in our system does not appear to be reversible; this suggests it should be considered as a type of catastrophic inversion provoked by the presence of hydrophilic surfactant rather than a transitional inversion.

W/O \rightarrow O/W phase inversions caused by adding hydrophilic surfactant do not necessarily give small droplets but we have observed fine emulsions in some systems. This is currently being studied in more detail. It is hoped that improved understanding of the fundamental phenomena will show how formulations can be systematically optimised to give small droplet sizes.

Acknowledgements

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